

Distribution of POC, PON, and particulate Al, Cd, Cr, Cu, Pb, Ti, Zn and $\delta^{13}\text{C}$ in the English Channel and adjacent areas

Trace metals
C, ^{13}C , N
Suspended matter
Channel

Métaux traces
C, ^{13}C , N
Matière en suspension
Manche

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ABSTRACT

A study of the spatial distribution of the total suspended matter and of its elemental composition (C, N and trace metals) has been performed in the English Channel, the Celtic Sea, and the Southern Bight of the North Sea in June and October 1991. South-west to north-east gradients of suspended matter mass and of lithogenic components (Ti and Al) linked to riverine inputs and to depth shallowing, are observed; organic carbon and nitrogen display an opposite distribution pattern and reach a maximum in the Biscay oceanic waters. Cu, Pb and Zn concentrations are highest near industrialized areas and large estuaries, showing the importance of river inputs. In contrast, Cd, Cu and Cr concentrations are markedly elevated in organic-rich suspended matter from waters in which suspended matter loadings are low, suggesting a significant biological uptake. Finally, $^{13}\text{C}/^{12}\text{C}$ analyses reveal the relative importance of coastal or continental inputs in the north-eastern Channel and in the North Sea.

RÉSUMÉ

Distribution du carbone et de l'azote organique, de Al, Cd, Cr, Cu, Pb, Ti, Zn et du $\delta^{13}\text{C}$ de la matière particulaire dans la Manche et les régions adjacentes.

Une étude de la répartition spatiale de la matière en suspension et de sa composition élémentaire (C, N et métaux traces) a été réalisée dans la Manche, la Mer Celtique et la Baie Sud de la Mer du Nord en juin et octobre 1991. Il existe un gradient du sud-ouest vers le nord-est en masse de matériel particulaire et en composés lithogéniques (Ti et Al), lié aux apports fluviaux et à la diminution de la profondeur; une distribution inverse s'observe pour les traceurs organiques (C et N) qui sont plus abondants dans les eaux océaniques. Certains métaux (Cu, Pb, Zn) présentent des concentrations maximales au voisinage des zones industrialisées et des estuaires. Par ailleurs Cd, Cu et Cr apparaissent en concentration plus importante dans la matière particulaire des eaux faiblement chargées en suspensions, mais riches en matière organique, suggérant une absorption active par la matière vivante. Enfin, une analyse des rapports isotopiques $^{13}\text{C}/^{12}\text{C}$ a permis de mettre en évidence l'importance des apports terrestres ou côtiers au nord-est de la Manche et en Mer du Nord.

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INTRODUCTION

During the past decade, with the development of accurate methods of sampling and determination of low concentration levels of trace elements in sea water, significant advances have been made in evaluating the temporal and spatial distribution of heavy metals on the North-western European Continental Shelf. But if many data are now available for certain areas, *i.e.* mainly the North Sea (Duiniker and Nolting, 1977, 1982; Balls, 1985a, 1985b; Mart and Nürnberg, 1986; Nolting, 1986; Baeyens *et al.*, 1987; Eisma and Kalf, 1987; Nolting and Eisma, 1988; Fileman *et al.*, 1991; Kersten *et al.*, 1991; Bouquegneau *et al.*, 1992) and the waters adjacent to the British Isles (Kremling, 1983; Jones and Jefferies, 1983; Kremling and Hydes, 1988; Harper, 1988, 1991), data concerning the English Channel mainly deal with dissolved material and are relatively scarce despite the impact of human activity on this area (Kremling, 1985; Kremling and Pohl, 1989; Tappin *et al.*, 1993).

Suspended matter, however, plays major roles in the oceanic cycle of many elements. As a direct food source for many herbivorous and suspension- or detritus-feeders, either benthic or planktonic, it directly influences trace element concentrations in the higher trophic levels of oceanic food webs. The flux of particles from surface to deep-ocean waters also directly affects the composition of both sea water and bottom sediments due to scavenging processes.

The present paper describes the results of investigations concerning suspended material collected at 36 locations during summer and autumn 1991 in both the English Channel and two adjacent areas, the Southern Bight of the North Sea and the Celtic Sea. This region, interfacing the deep Atlantic Ocean and the shallow North Sea, is characterized by highly complex hydrological mesoscale processes (Salomon and Breton, 1991; Delhez and Martin, 1992) including local gyres, important river inputs (*e.g.* Ems, Rhine, Meuse, Scheldt, Thames, Solent, Seine, Somme),

and moving frontal zones (Ushant, Chapelle Bank, Straits of Dover; Sournia *et al.*, 1990). Moreover, this area could be the site of significant atmospheric inputs of different pollutants from the highly urbanized and industrialized surrounding countries. Besides analyses of heavy metal content, this paper also presents data on organic carbon and nitrogen content and on carbon stable isotope ratios of suspended matter, the study of which constitutes a fruitful method for discriminating between different sources of POM (Sackett, 1989).

MATERIAL AND METHODS

The samples were collected during both the 1991 cruises of the R.V. *Belgica*: campaign 91/16 (24 June to 9 July) in the English Channel, Northern Biscay and Celtic Sea (Fig. 1, points 10 to 36), and campaign 91/22 (21 to 30 October) in the Southern Bight of the North Sea (Fig. 1, points 1 to 9). Suspended Particulate Matter (SPM) was sampled by centrifugation, using an α -Laval purifier (model MAB 104) filtering sea water pumped with a delivery adjusted at about 1 m³.h⁻¹ at 3 m depth at the ship's hull. Sampling was done either at some fixed stations (triangles on Fig. 1) or while steaming between two stations (lines on Fig. 1). Metal concentration measurements are in the latter case average values over transects ranging from 50 to 200 km in length (precise positions are listed in Table 1). Filtering times were adjusted to avoid clogging of the apparatus and were of the order of: 3-4 hours in the Eastern Channel and the North Sea, less than 1 hour in the vicinity of estuaries, and between 6 and 10 hours in the western areas. In the present paper, stations were renumbered in a logical sequence from Dogger Bank to the Celtic Sea without considering the actual ship route.

All the samples were frozen after collection. After weighing, they were divided into several subsamples for the

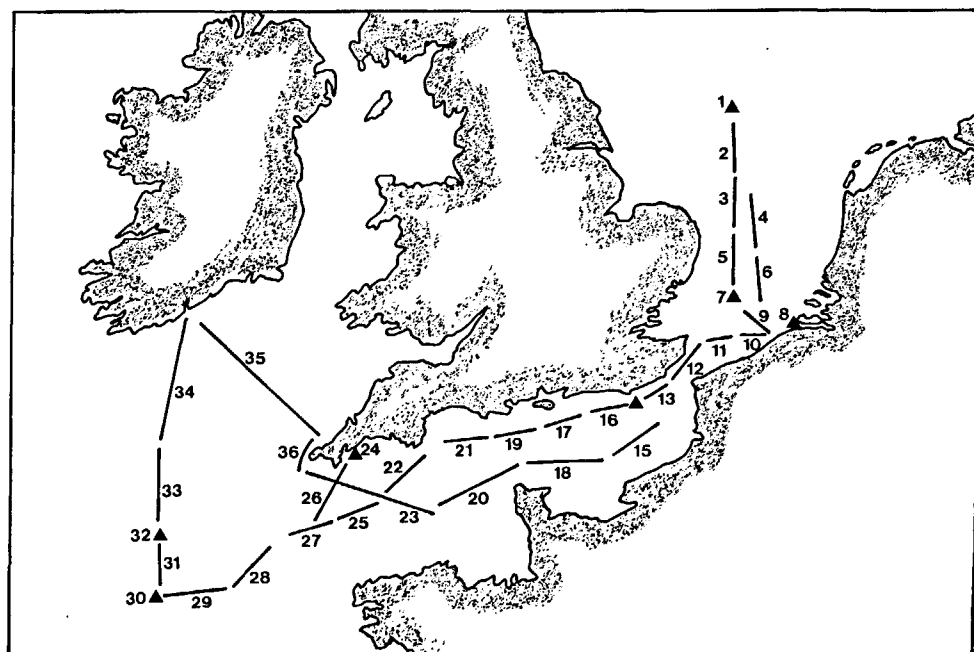


Figure 1
Position of sampling transects (—) or stations (▲).
Position des trajets (—) et stations (▲) de prélèvement.

Table 1

Sampling positions, mean bottom depths, physico-chemical parameters (mean values), SPM concentrations and associated C-N contents and $\delta^{13}\text{C}$.

Positions des prélèvements, profondeurs moyennes, valeurs moyennes des paramètres physico-chimiques, concentrations en matériel particulaire et contenu en C-N et $\delta^{13}\text{C}$ associés.

Station	Position	Depth m	Salinity psu	Temp. °C	Nitrates µMol	Chloro a µg/l	TSM	C cont.	N cont.	C/N ratio	$\delta^{13}\text{C}$
							mg/l	%	%		‰
1	53°36'N-2°41'E	22	34.7	13.4		0.85	7.4	6.1	0.6	10.6	-22.4
2	53°30'N-2°32'E > 52°57'N-2°29'E	27	34.6				11.3	3.7	0.2	18.5	-21.4
3	52°50'N-2°29'E > 52°22'N-2°28'E	35	34.4				8.4	4.9	0.3	17.6	-21.0
4	52°47'N-2°38'E > 52°25'N-2°38'E	29	34.3				9.9	4.4	0.2	22.8	-19.8
5	52°17'N-2°28'E > 51°45'N-2°35'E	23	34.3				8.3	6.4	0.5	13.0	
6	52°22'N-2°38'E > 52°01'N-2°38'E	21	34.3				4.6	6.3	0.5	11.5	-22.2
7	51°29'N - 2°30'E	14	34.9	14.2			5.1	10.3	1.3	8.0	-20.9
8	51°25'N - 3°39'E	10	31.0	12.3			1.43				
9	51°20'N-3°10'E > 51°29'N-2°30'E	15	32.7				110.0	4.7	0.1	68.2	-18.7
10	51°23'N-3°00'E > 51°20'N-2°30'E	11	34.2	13.6	2.01	2.07	99.1	6.3	0.3	21.8	-20.8
11	51°20'N-2°30'E > 51°20'N-2°08'E	24	34.8	12.8	0.11	1.24	4.1	15.9	2.4	6.6	-20.4
12	51°20'N-1°50'E > 50°50'N-1°00'E	34	35.2	12.2	0.11	0.95	2.0	13.1	1.8	7.3	-18.5
13	50°50'N-1°00'E > 50°40'N-0°30'E	29	35.2	11.9	0.12		1.9	17.0	2.3	7.4	-19.0
14	50°41'N-00°30'E	28	35.2	11.9	0.12	0.98	2.8	12.4	1.6	7.6	-19.1
15	50°25'N-0°57'E > 50°01'N-0°04'W	41	35.0	13.5	1.15	1.81	2.6	13.0	1.8	7.1	-18.9
16	50°41'N-0°30'E > 50°30'N-0°39'W	41	35.1	12.5	0.12	0.98	3.8	16.7	2.5	6.8	-20.4
17	50°30'N-0°39'W > 50°20'N-1°35'W	52	35.2	12.7	0.30	0.54	1.2	16.6	2.5	6.7	-19.4
18	50°00'N-0°15'W > 50°02'N-1°40'W	60	35.0	13.1	1.95		1.3	11.2	1.5	7.6	-18.6
19	50°20'N-1°35'W > 50°15'N-2°30'W	52	35.3	12.1	0.40	1.98	0.8				-20.8
20	50°00'N-1°49'W > 49°30'N-3°30'W	86	35.2	12.6	3.35	0.74	1.6	11.7	1.8	6.6	-17.6
21	50°15'N-2°30'W > 50°05'N-3°30'W	58	35.3	11.9	0.76	1.82	1.9	21.4	3.2	6.7	-23.2
22	50°05'N-3°30'W > 49°44'N-4°20'W	66	35.3	12.5	0.73	1.99	1.6	18.1	3.3	5.5	-19.4
23	50°00'N-6°00'W > 49°30'N-3°30'W	101	35.1	12.8		1.94	2.0	17.4	2.8	6.3	-21.3
24	50°08'N-5°05'W	10	35.3			1.20	1.3	28.7	5.1	5.6	-21.9
25	49°44'N-4°22'W > 49°25'N-5°04'W	87	35.3	13.4	0.18	0.96	1.6	21.1	3.1	6.9	-21.6
26	49°25'N-6°30'W > 50°06'N-5°00'W	77	35.3				1.7	24.1	3.5	6.9	-22.8
27	49°25'N-5°04'W > 49°05'N-6°10'W	107	35.4		0.10	0.96	1.8	30.2	5.1	5.9	-23.1
28	48°56'N-6°01'W > 48°20'N-6°30'W	127	35.5	13.9	0.07	0.48	2.0	32.9	6.0	5.5	-22.5
29	48°20'N-6°30'W > 48°09'N-8°14'W	340	35.6	14.1	0.41		1.1	14.2	1.9	7.6	-20.3
30	48°09'N-8°20'W	1200	35.6	14.2	0.71	1.26	1.4	24.9	3.8	6.5	-24.5
31	48°09'N-8°29'W > 49°00'N-8°33'W	475	35.5	14.4	0.38		1.7	26.7	3.2	8.4	-23.7
32	49°00'N-08°22'W	155	35.5	14.5	0.07	0.28	1.1	30.1	3.6	8.3	-21.8
33	49°04'N-8°11'W > 50°30'N-8°30'W	130	35.4	14.7	0.10	0.35	0.5	28.5	3.8	7.6	-23.9
34	50°30'N-8°30'W > 51°45'N-8°20'W	65	35.3	14.8			0.6	20.2	2.1	9.7	-24.1
35	51°45'N-8°15'W > 50°15'N-5°40'W	65	35.2	13.6			0.6	25.3	3.7	6.7	-20.9
36	50°15'N-5°40'W > 50°00'N-6°00'W	48	35.3	12.3		2.01	1.0	23.2	3.4	6.8	-21.5
							1.3	20.6	2.8	7.3	-18.1

analysis of trace metals, carbon and nitrogen content, and $\delta^{13}\text{C}$ ratios.

For heavy metal determination, a 100 mg subsample, dried at 50°C, was inserted into a PTFE bomb. Three ml of concentrated HNO_3 , 2 ml of concentrated HCl , 1 ml of concentrated HF (35%) and 1 ml of H_2O_2 were added to the solid material. The bomb was then closed (tightened at 17 N), and heated by steps up to 600 W in a MLS-1200 Milestone microwave oven. The cover was removed, the solution was subsequently evaporated to dryness, and then redissolved in 4 ml of a mixture of diluted HNO_3 and HCl (+ 0.2 g of H_3BO_3 to avoid precipitation of insoluble fluoride). This solution stood overnight and then was brought to 15 ml. Analyses were carried out by Inductively Coupled Argon Plasma Spectrometry (A.R.L. 3510). The quality of our data was controlled using standard reference sediments, and an intercomparison of our measurements was made with those obtained by the Laboratories of Chemical Oceanography (*R. Wollast* - ULB) and of Analytical Chemistry (*W. Baeyens* - VUB) of the Free University of Brussels (Belg.) on similar material collected at several stations, analyzed by other techniques (AAS) (*Dauby et al.*, 1993). For later discussion, metal data will be expressed either as mass ratios ($\mu\text{g}_{\text{metal}} \cdot \text{g}_{\text{solid}}^{-1}$) or as enrichment factors, defined as: $E_f = ([\text{metal}]/[\text{Al}])_{\text{sample}} / ([\text{metal}]/[\text{Al}]_{\text{crust}}$. These E_f are calculated using the com-

position of average crust (given by *Martin and Meybeck*, 1979) which is considered to represent the reference situation with no metal excess.

The subsample allocated to C-N content and stable carbon isotope ratio measurements was first slightly acidified with HCl to remove carbonates; it was rinsed, oven-dried at 55°C for several days and ground into fine powder. Determinations of POC and PON were performed on 1 to 3 mg of dried material with a Carlo Erba elemental analyzer, model NA 1500. For $\delta^{13}\text{C}$, material was first vacuum-sealed with copper oxide wire in a Pyrex flask (*Sofer*, 1980); flasks were kept in a furnace at 550°C for one day to achieve the complete combustion of the organic matter. Produced CO_2 was then collected using a liquid nitrogen gas-trapping apparatus. Determinations of $\delta^{13}\text{C}$ values were performed with a Varian Mat CH5 Isotope Ratio Mass Spectrometer. All values are reported relative to the international PDB standard as

$$\delta^{13}\text{C} = [(R_{\text{sample}} / R_{\text{standard}}) - 1] \times 1000,$$

where R is the $^{13}\text{C}/^{12}\text{C}$ ratio. Routine measurements are accurate to within $\pm 0.3\text{‰}$.

Water was also collected at each sampling station in order to determine the chlorophyll *a* concentrations, using the classical method described by *Lorenzen and Jeffrey* (1978).

RESULTS AND DISCUSSION

SPM concentrations – C, N, and chlorophyll contents

Material collected by flow through centrifuge is representative of the smaller-sized particles composing the bulk of SPM, as was shown by Dehairs *et al.* (1985) who compared similar material either centrifuged or collected by filtration over 0.45 µm porosity Millipore membranes. Data on SPM concentrations for the whole studied area are listed in Table 1 and shown on Figure 2. SPM concentrations are quite constant throughout the English Channel (from 0.8 to 3.8 mg.l⁻¹, average: 1.8 mg.l⁻¹), with a maximum north of the Seine Bay. The values recorded in the Straits of Dover are in good accordance with the data of Dupont *et al.* (1993). In the Celtic Sea, concentrations are much lower (about 0.6 mg.l⁻¹), displaying the oligotrophic feature of the nearby Biscay waters, but become relatively more important in the vicinity of the La Chapelle Bank shelf-break (point 30), which corroborates previous data of Pingree *et al.* (1982). In the Southern Bight of the North Sea, the observed SPM concentrations become much higher, up to 12 mg.l⁻¹, due to the considerable terrigenous inputs via the Scheldt, Thames, Meuse, Rhine and other less important river estuaries, and also to resuspension processes. These data are in good agreement with those of Duinker and Nolting (1977), Dehairs *et al.* (1985), or Eisma and Kalf (1987). The latter found SPM concentrations greater than 40 mg.l⁻¹ in front of the Zeeland Delta, where we observed maximal values (up to 110 mg.l⁻¹).

POC content (expressed as % of SPM) displays strong variations according to the sampling area (Table 1 and Fig. 3). In the Southern Bight of the North Sea, percentages are quite low, ranging from 3.7 to 6.4 (except at St. 7), displaying a high mineral content of suspended material. These values are, however, higher than those measured by Eisma and Kalf (1987, ≈ 2% in January, when plankton population was sparse) or Kersten *et al.* (1991), but they were obtained in October during a small phytoplankton bloom (mainly *Coscinodiscus* diatoms). The low observed organic matter content of North Sea surface water SPM reflects both the shallow depth which favours resuspension processes and the bulk of land-originated material injected into the sea through the deltas. Throughout the English Channel, an increasing POC percentage gradient is observed from east to west (except in the area of the Isle of Wight, influenced by the Avon and Solent Rivers), concurrently with deepening which attenuates resuspension. Everywhere in the Celtic Sea (except at St. 28 which will be discussed further), POC percentages are quite high, ranging from 25 to 33%, suggesting an organic (plankton)-rich SPM and a quasi-absence of terrigenous inputs.

Difference in the sampling period (autumn for North Sea stations, summer for the others) appears however to have little influence on the organic content of collected surface SPM. As shown by chlorophyll values and by comparison with other data sets obtained during *e.g.* spring cruises in the same area (Dauby *et al.*, unpubl.), both cruises occur outside any important plankton bloom; at the most, the small diatom bloom observed in the Southern Bight should

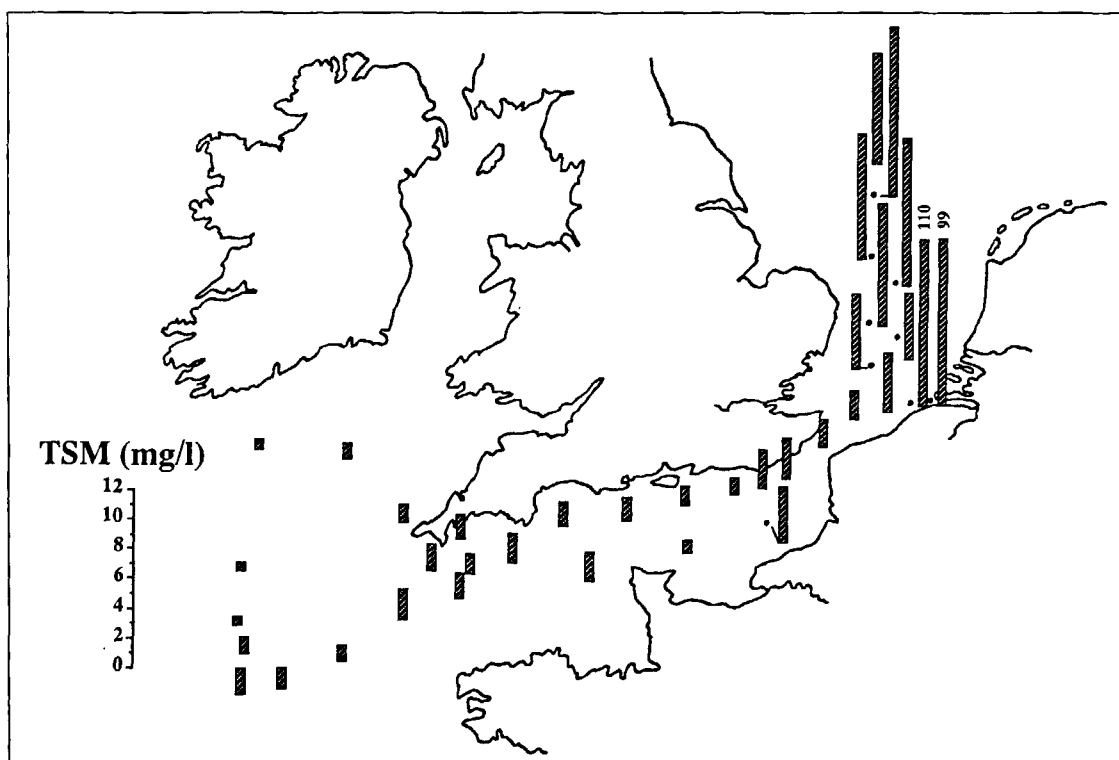


Figure 2
 Surface SPM distribution (mg.l⁻¹).
 Distribution du matériel particulaire (mg.l⁻¹) des eaux de surface.

only lead to a weak relative increase of the SPM organic fraction with respect to the mineral one.

PON percentages display the same distribution pattern as those for POC (Tab. 1), with very low values (down to 0.2 %) in the North Sea, and larger values (up to 6 %) in the eastern Channel and the Celtic Sea.

In the plotting of POC and PON percentages *versus* SPM concentrations (Fig. 4), two logarithmic negative relationships clearly appear, displaying the great importance of the mineral fraction in the waters highly loaded in suspended matter. The respective equations of both the slopes are:

$$\text{Log C} = 1.4201 - 0.081 \text{ SPM} \quad (r^2 = 0.77)$$

$$\text{Log N} = 0.6508 - 0.0012 \text{ SPM} \quad (r^2 = 0.82)$$

where C and N are in %, and SPM in mg.l^{-1} . It is noteworthy that the PON slope is significantly steeper, which leads to highest C/N ratios for high SPM concentration values. A similar negative relationship – although linear – between particle concentration and its organic content was also observed for North Sea surface SPM by Kersten *et al.* (1991). The difference in the shape of the relationships (log-linear *vs* linear) could be explained by the fact that our survey covered a larger geographical area, including the oligotrophic Celtic Sea where SPM concentrations are particularly low and organic-rich.

Throughout the English Channel and the Celtic Sea, C/N ratios are not far from the classical REDFIELD ratio (106:16 for phytoplankton-based suspended matter), but generally a little higher, as was also measured by Copin-Montégut and Copin-Montégut (1983) along Northern African Atlantic coasts. In the Southern Bight, however, C/N ratios are surprisingly high, reaching values around 20

(and up to 68 at St. 8!). These figures, even greater than those recorded for N and P-depleted lakes (Hecky *et al.*, 1993), can only be explained by a combination of different factors such as: (i) the complexity of the pelagic food web in very shallow waters, with an important microbial loop generating a large amount of C-enriched dead organic matter; (ii) an input of N-depleted detrital flocs via riverine inflows; or (iii) a rapid turnover rate and strong competition for nitrogen within the water column food-web.

Chlorophyll *a* data (Fig. 3 and Tab. 1) corroborate POC information, as pigment *vs* organic carbon ratios are quite small in the oceanic part of the studied domain, and maximum in the North Sea. These high Chl*a*/C ratios reflect the importance of the dead organic matter (as also shown by phaeopigments data, Dauby *et al.*, unpubl.) in the bulk of SPM; this detrital matter can come either from land inputs, but also from resuspension processes which bring sedimentary organic carbon up to surface waters. It is worth observing that in front of Le Havre and along the English coast of the Channel, Chl*a*/C ratios are also high, displaying respectively the terrigenous input of the Seine River and that from the different inlets of Eastern Cornwall, Hampshire and Sussex.

$^{13}\text{C}/^{12}\text{C}$ ratios

Stable carbon isotope ratios can fruitfully be used in SPM analyses as they reflect the origin(s) of that matter. Carbon isotope fractionation by plants during photosynthesis is not a constant and is dependent upon both the metabolic pathway involved and the nature of the inorganic substratum. A consequence is the formation of several carbon reservoirs with distinct $\delta^{13}\text{C}$ values, which constitutes so many star-

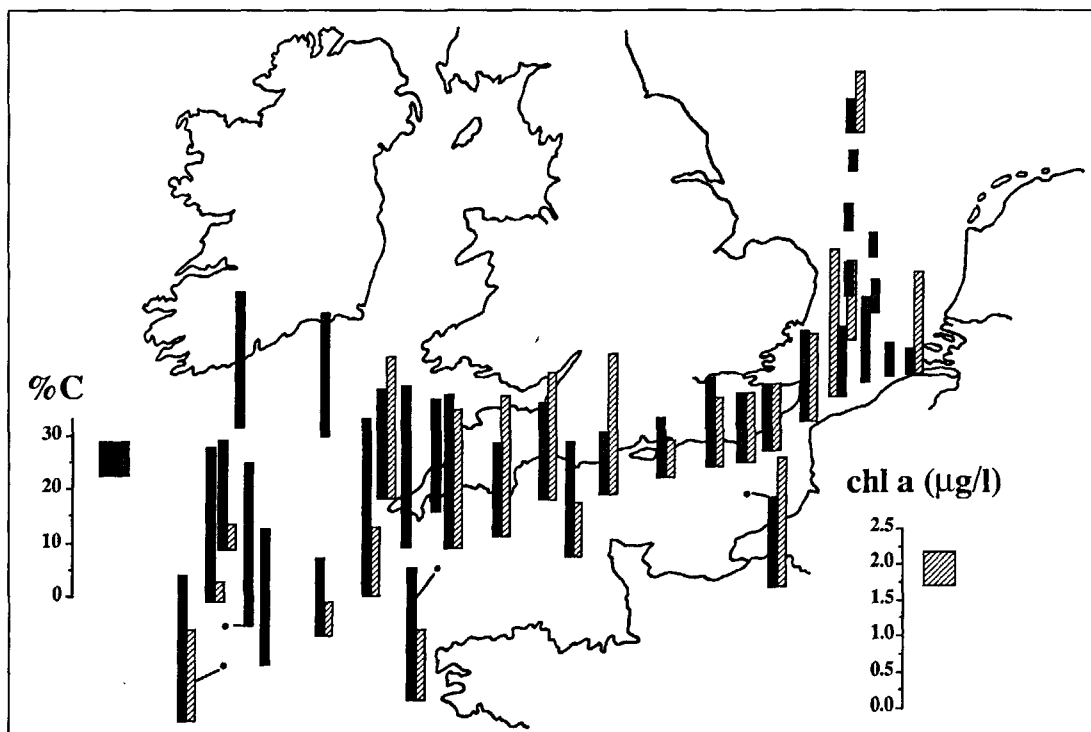


Figure 3

Distribution of chlorophyll *a* ($\mu\text{g.l}^{-1}$, hatched) and of POC (% of total suspended matter, dark).

Distribution de la chlorophylle *a* ($\mu\text{g.l}^{-1}$, hachuré) et du carbone organique particulaire (% de la matière particulaire totale, noir).

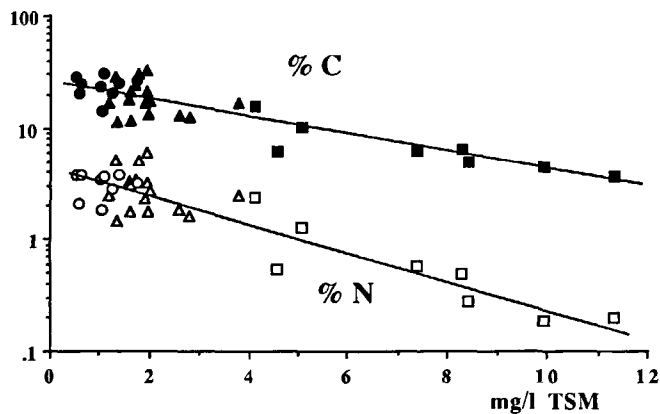


Figure 4

Relationships between SPM concentrations (mg.l^{-1}) and respectively POC and PON (% of total suspended matter, log scale). Circles: Celtic Sea; triangles: English Channel; squares: North Sea. Data for Scheldt mouth (St. 8 and 9) have been disregarded.

Relations entre la concentration en matériel particulaire (mg.l^{-1}) et respectivement le carbone et l'azote organiques particuliers (en % du matériel total, échelle log). Cercles: Mer Celtique; triangles: Manche; carrés: Mer du Nord. Les données de l'embouchure de l'Escaut (St. 8 et 9) n'ont pas été prises en considération.

ting points of food webs, *e.g.* as particulate organic matter in marine environments.

In the prospected area, the natural potential carbon sources are: (i) terrestrial plant material (mainly of C3-pathway at our latitudes $-\delta^{13}\text{C}$ of about -26‰) entering the sea as detritus via estuaries; (ii) phytoplankton, with temperature-dependent $\delta^{13}\text{C}$ values (about -23‰ in considered waters, Fontugne and Duplessy, 1981); and (iii) marine plants, with higher $\delta^{13}\text{C}$, ranging from about -10‰ (seagrasses) to about -20‰ (seaweeds) (Dauby, 1989); to these natural sources must be added anthropogenic ones (such as crude oil-derivatives or sewage effluents).

The $\delta^{13}\text{C}$ of analyzed SPM range from -17.6‰ west of the Isle of Wight to -24.5‰ in the north of Biscay (*cf.* Tab. 1). These data fit well into the range of those presented for North Sea marine and estuarine POC by Salomons and Mook (1981), Eisma *et al.* (1982), Laane *et al.* (1990) or Dauby *et al.* (1992) who reported $\delta^{13}\text{C}$ values ranging from -14.0 to -27.4‰ . Minimum values (the most depleted in ^{13}C , -22 to -24‰) are observed on both boundaries of the studied domain, *i.e.* the Celtic Sea and the Dogger Bank, and indicate phytoplankton-based ecosystems. The less depleted values (-17.6‰) are measured in the centre-north of the Channel, near Southampton, but do not correspond to any peculiarly low POC/PON ratio as shown by Faganeli *et al.* (1994) for the Adriatic Sea; they tag an important input of coastal material. This may consist of plant-originated matter (seagrass detritus, Laane *et al.*, 1990) or be associated with man-originated organic waste pollution (Tan and Walton, 1975), but is not derived from petroleum which $\delta^{13}\text{C}$ is far lower (see *e.g.* Spies and DesMarais, 1983). Between central Channel and both the north-easter and south-western extremities, a relatively constant gradient of $\delta^{13}\text{C}$ is observed.

Lithogenic components: Aluminium and Titanium

The distribution of Al concentrations is very similar to that of SPM (Fig. 5) since particulate aluminium is mainly injected into ocean waters via terrigenous material and does not dissolve in sea water at a significant rate (Kremling, 1985).

Al concentration values are quite similar all along the Channel, albeit with concentrations two to three times higher along the English coast (ranging from 2 to 16.6 mg.g^{-1}) than along the French one; these data are in good agreement with those given by Dehairs *et al.* (1985) who found a range of 5.5 to 17.1 mg.g^{-1} depending on the size fraction. It is also noteworthy that there is no significant difference in particulate Al concentration values through the Straits of Dover, contrary to findings in the dissolved phase by Chou and Wollast (1993) who suggest a sea water flow from the North Sea into the Channel.

In front of the Belgian coast (St. 8 to 10), near the Scheldt mouth, measured concentrations are a little higher (11 to 23 mg.g^{-1}), as a consequence of the riverine input. These values agree with those reported by Regnier and Wollast (1993) (about 25 mg.g^{-1} at the saline end member) who observed a conservative dilution behaviour for Al from fresh to sea water.

In the North Sea, values become much higher, greater than 20 mg.g^{-1} and attaining 70 mg.g^{-1} in front of the Rhine Estuary. High concentrations were also reported by Duinker and Nolting (1977) – about 30 mg.g^{-1} –, by Baeyens *et al.* (1987) – from 4 to 20 mg.g^{-1} –, but northwards, at the Dogger Bank, Dehairs *et al.* (1985) and Fileman *et al.* (1991) observed mean lower Al concentrations (respectively 0.46 and 2.5 mg.g^{-1}). Our peculiarly high values could be explained by the stormy weather prevailing before the October cruise, which in all likelihood induced resuspension of sediments, and especially of fine material in which Al content is often increased (Windom *et al.*, 1989); significant elevations of Al concentrations associated with storm conditions were recently reported by Fileman *et al.* (1991) for that area.

Concentrations in the Celtic Sea are much lower, averaging 1.1 mg.g^{-1} , reflecting the oceanic origin of the suspended matter there.

Assuming an Al weight content of 15% in aluminosilicates, we may evaluate the proportion of terrigenous clay making up the SPM. It appears (frame in Fig. 5) that the clay percentage increases for high loads of suspended matter in sea water (up to 45% at St. 6, North Sea area), that is in good agreement with POC and PON data. This observation is linked to the vicinity of large estuaries and with the resuspension processes in that shallow basin.

The distribution of Ti concentrations in SPM is very similar to that of aluminium (Fig. 6) as confirmed by the relative constancy of the Ti/Al ratios (around 0.04).

Despite the fact that at least four dumping sites of titanium dioxide production waste (more than 1,000,000 tons.yr $^{-1}$, Weichart, 1973) have been extensively exploited up to the beginning of the 1980s in the area between Dunkirk and The Hague, no particular anomaly can be observed either in Ti/Al ratios or in the Ti E_f factor in that area (Figs. 6 and 12), although Ti concentrations in SPM are higher than in

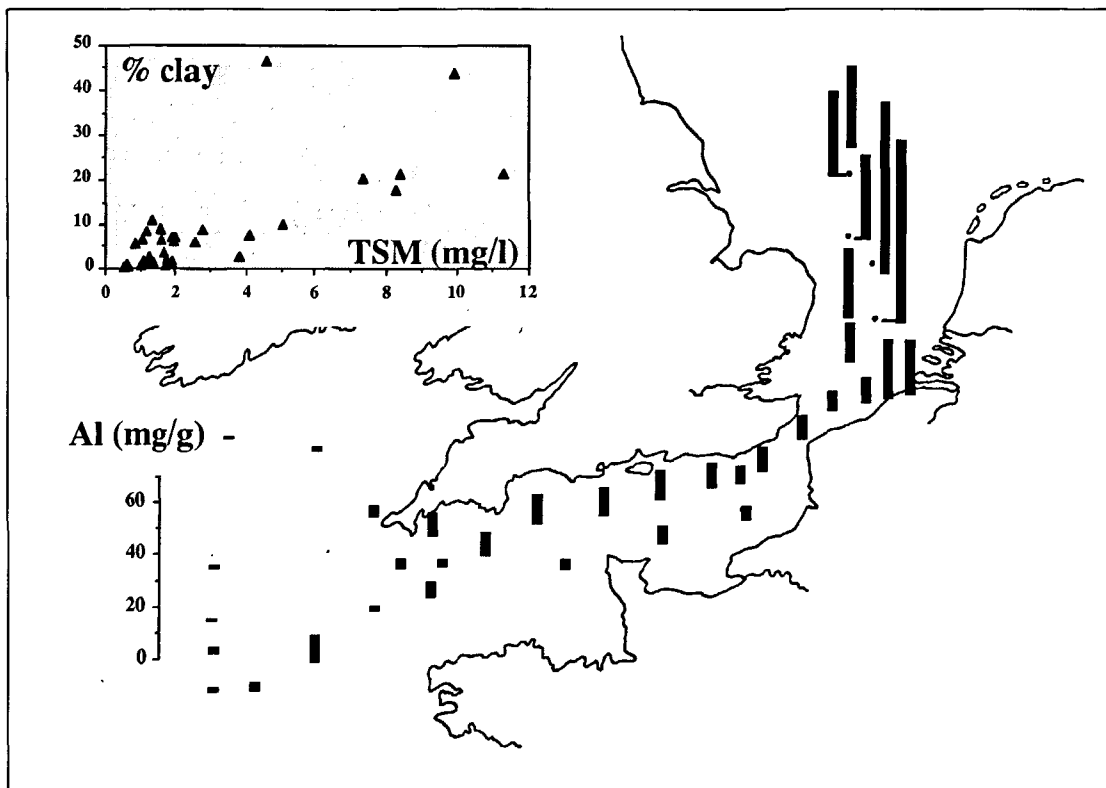


Figure 5

Distribution of particulate Al ($\text{mg}\cdot\text{g}^{-1}$). Relationship between SPM concentrations and percentages of clay in SPM estimated from Al data (St. 8 and 9 omitted).

Distribution de l'Al particulaire ($\text{mg}\cdot\text{g}^{-1}$). Relation entre concentrations en matériel particulaire total et pourcentages d'argile dans celui-ci estimés sur base des données d'Al (sans les St. 8 et 9).

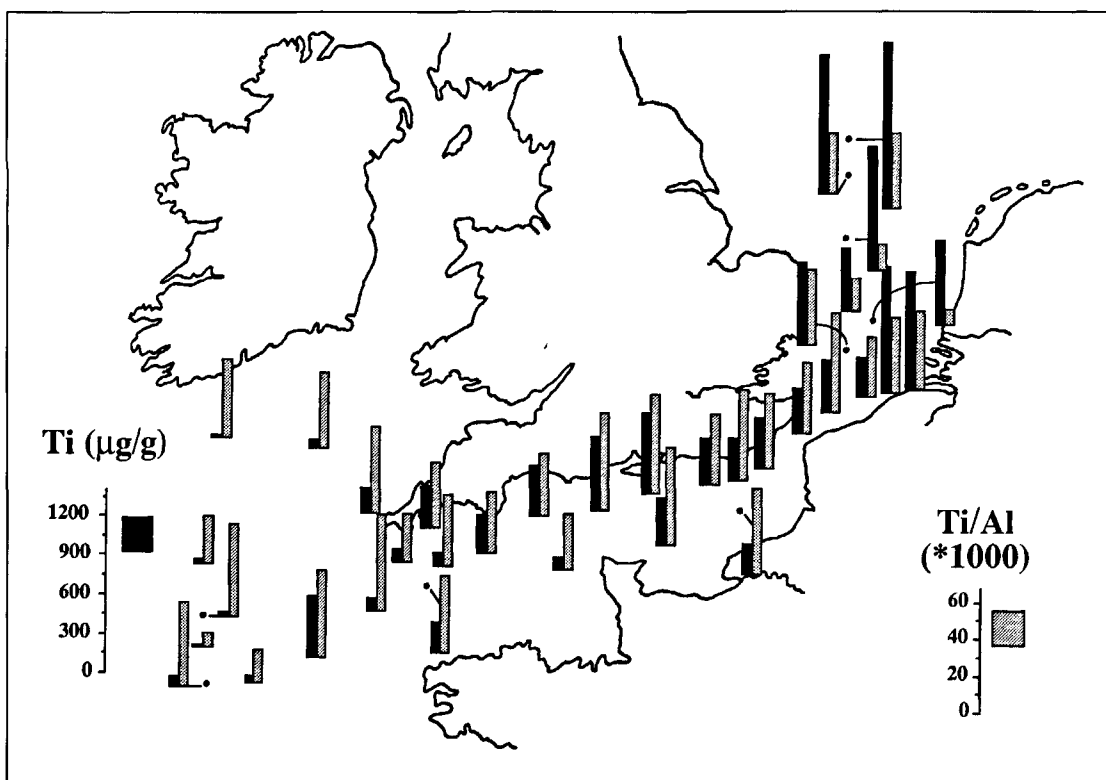


Figure 6

Ti: distribution of particulate metal ($\mu\text{g}\cdot\text{g}^{-1}$, black) and of ratios normalized with respect to Al (grey).

Ti : distribution du métal particulaire ($\mu\text{g}\cdot\text{g}^{-1}$, noir) et du rapport Ti/Al (grisé).

the eastern Channel. The latter remain high throughout the Southern Bight, reaching 1.2 mg.g^{-1} ; they are about three times greater than those measured by Nolting and Eisma (1988) in the same area, but remain far removed from average river values (5.6 mg.g^{-1} , Martin and Meybeck, 1979) and close to average crustal ones (E_f factor ≈ 1).

The very low concentrations encountered in the Celtic Sea confirm the importance of organic vs detritic material in that region.

Copper and Chromium

Within the area surveyed, both the metals Cu and Cr have relatively the same distribution pattern.

Copper is the better studied metal and considerable data has been published about its concentration in the particulate phase (*see* Tab. 3). Our measurements (Fig. 7) show minimum values in the western and central parts of the Channel, with about $20 \text{ }\mu\text{g.g}^{-1}$ (round 35 ng.l^{-1}) on the average. In the northeastern Channel, Cu concentrations increase towards the English coast (especially off Southampton), indicating a land-based source of copper, doubtless related to the Hampshire and Sussex chemical and metallurgical industrial complexes. Concentrations decrease in the Straits of Dover area, and then rise again in front of the Zeeland deltas, reaching up to $200 \text{ }\mu\text{g.g}^{-1}$ at St. 6. These high values are obviously related to estuarine inputs, but the non-negligible release of copper from shelf sediments must also be taken into account (Kremling, 1983; Balls, 1985*b*). The data obtained from the south Dogger Bank and those from *e.g.* Fileman *et al.* (1991) or Mart and Nürnberg (1986) support this opinion. In the North Sea, copper seems to be closely associated with sus-

pended matter inputs (either land-originated or mainly linked with resuspension and remobilization processes, as was shown by Paulson *et al.*, 1991, with an active role of benthic biogenic particles, Duinker and Nolting, 1977). In any case, our data fit well into the range of previous measurements of the above-mentioned authors for North Sea and Channel areas. In the Celtic Sea, Cu content of SPM tends to increase, with values up to $50 \text{ }\mu\text{g.g}^{-1}$, in good agreement with the data on total Cu of Danielsson *et al.* (1985).

Chromium concentrations we measured are, as for copper, nearly constant throughout the English Channel (Fig. 8), averaging $19 \text{ }\mu\text{g.g}^{-1}$ ($\approx 30 \text{ ng.l}^{-1}$), far below mean river value ($70 \text{ }\mu\text{g.g}^{-1}$, Martin and Meybeck, 1979). They are, however, from two to ten times higher in the southern Bight, probably due to large riverine discharges. For the Celtic Sea stations, Cr concentrations are very high, up to $265 \text{ }\mu\text{g.g}^{-1}$, although metal amounts are not abnormally large (generally $< 0.07 \text{ }\mu\text{g.l}^{-1}$).

As previously observed, living organic matter seems to have a high affinity for both copper (Collier and Edmond, 1984) and chromium. This is confirmed by the fact that the high concentrations observed in the Celtic Sea, where POC percentages are maximum, are associated with peculiarly high metal/Al ratios (up to 0.14 for Cu, 0.2 for Cr), suggesting an uptake by living organic matter as phytoplankton. Such an uptake is also suggested when considering the E_f factors for both Cu and Cr (Fig. 12), markedly enhanced in Celtic Sea SPM samples. Copper is known for its ability to be bound to organic carrier sites (Collier and Edmond, 1983) and could be incorporated in diatom frustules (Martin and Knauer, 1973). Conversely, in the Southern Bight, metal/Al ratios are very low (less than $3 \cdot 10^{-3}$) and suggest a

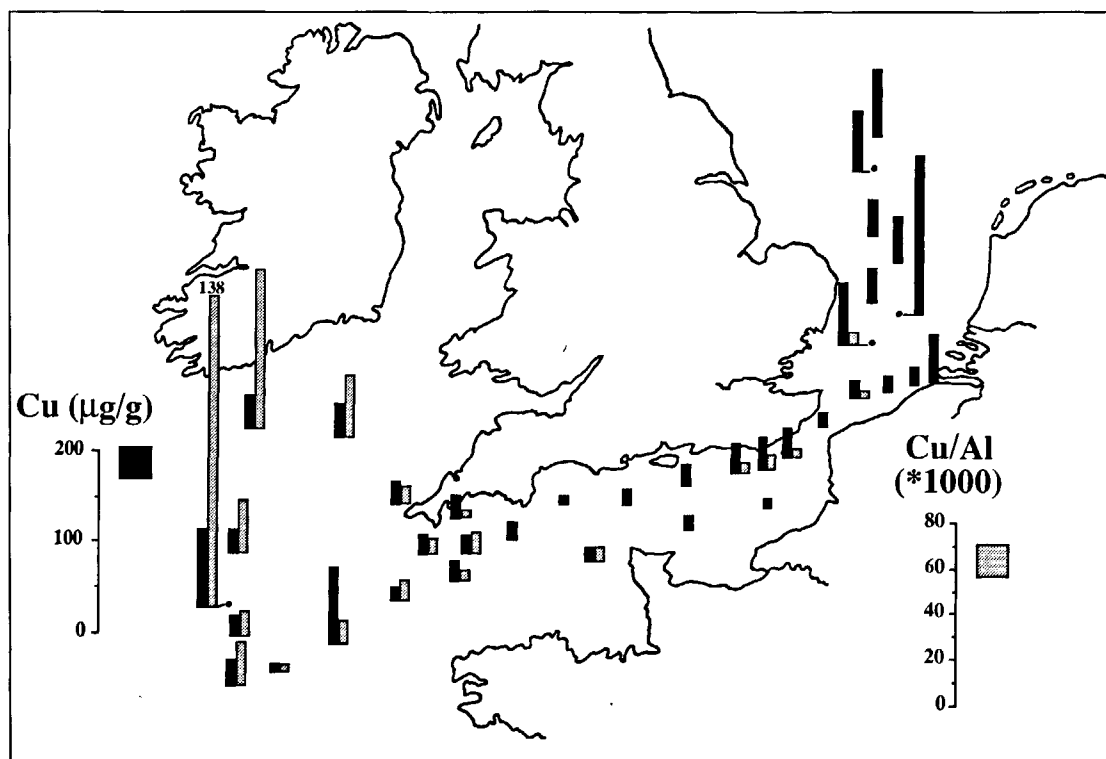


Figure 7

Cu: same as Fig. 6. Columns for Cu/Al ratios lower than 3×10^{-3} have not been drawn.

Cu: idem Fig. 6. Les barres des rapports Cu/Al inférieures à $3 \cdot 10^{-3}$ n'ont pas été représentées.

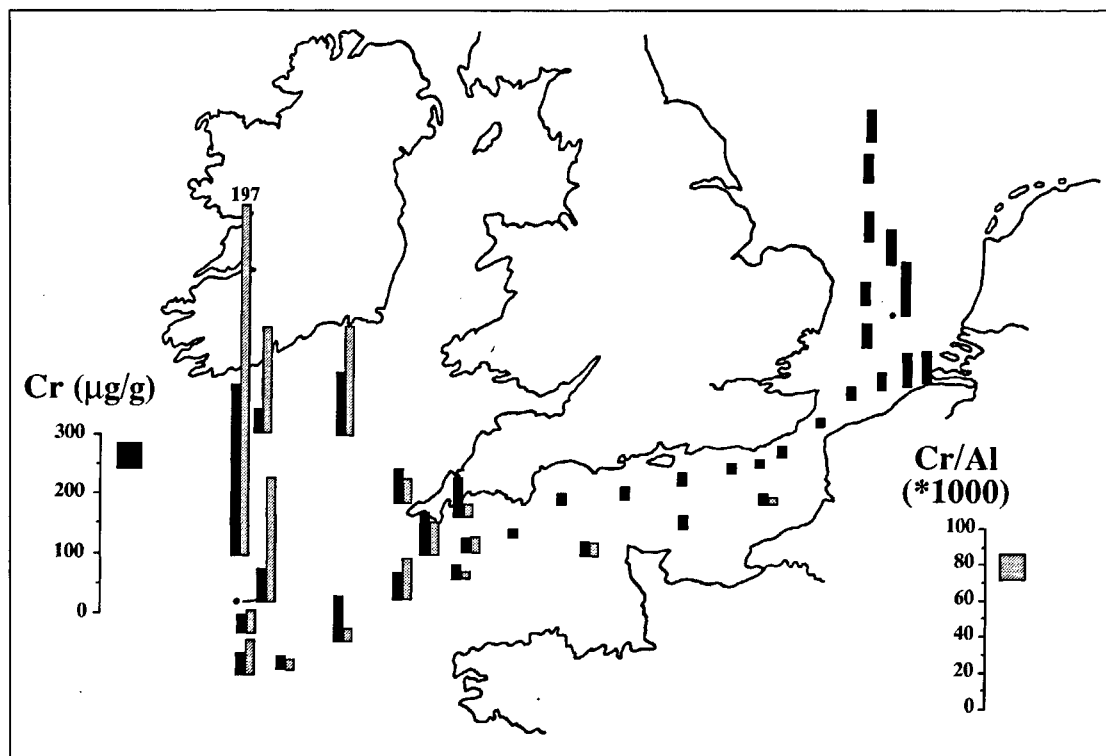


Figure 8

Cr: same as Fig. 6. Columns for Cr/Al ratios lower than 3×10^{-3} have not been drawn.

Cr: idem Fig. 6. Les barres des rapports Cr/Al inférieurs à $3 \cdot 10^{-3}$ n'ont été représentées.

weak adsorption on lithogenic particles; such low values were also reported by Nolting and Eisma (1988) for the whole North Sea.

Lead and Zinc

Like the previous two metals, Pb and Zn display a similar distribution pattern throughout the surveyed area.

Maximum Pb concentrations (disregarding St. 28) are observed off the Belgian coast, in front of Zeebrugge harbour (Fig. 9), as was previously noticed by Baeyens *et al.* (1985, 1987), and are probably the result of an input from the Scheldt (Gobert *et al.*, 1992). The association of Pb with a detritic and authigenic inorganic phase (mainly fine grained) has been invoked by Dehairs *et al.* (1985) considering a linear Pb/Al relationship from the Straits of Dover to the central North Sea; albeit less marked, such a relationship – and concurrently a negative Pb/POC one – are also observed from our data. Pb concentrations remain high in the whole Southern Bight and along the Channel English coast. This is in all probability linked to the high urbanization rate of the surrounding areas which produce large amounts of leaded aerosols, a predominant Pb source for the ocean (Buat-Ménard, 1983); moreover, shallow depths favour resuspension of sedimentary matter that can contain a significant amount of lead, easily scavenged at the sediment-water interface. The anthropogenic origin of Pb in the Channel is also suggested by its E_f factor (Fig. 12), the values of which are close to or greater than 10 throughout the area south of the Straits of Dover. Concentrations along the Channel French coast and in the Celtic Sea are general-

ly lower, except at St. 28 for which different 'anomalous' values have been recorded (Pb, Al, Cu, Ti, Zn, but also N, C and $\delta^{13}\text{C}$); this station is, however, far from known potential human inputs, and contamination due to a recent sewage release might be the source of such measured values. A direct contamination – affecting so many parameters – during sampling or analysis is hardly conceivable.

Among the studied elements, zinc is the metal that displays the highest concentrations except for the area situated north of the line joining the Rhine and Thames estuaries (*see* Fig. 10). These measurements fit quite well with those of Duinker and Nolting (1977) or Nolting (1986) for the Southern Bight, and those of Baeyens *et al.* (1985, 1987) for the Scheldt Estuary and the Belgian coast, but not with those of Dehairs *et al.* (1985) who found an increasing gradient from Channel waters to the central North sea. On the other hand, northern data from the Dogger Bank (Fileman *et al.*, 1991), if somewhat lower, correspond better to ours. Channel Zn concentrations present two relative maxima, one easterly, in front of the Hampshire coast, and the other westerly, off the Cornish coast, which could be related to riverine inputs. As was noticed for lead, zinc E_f factors significantly increase in the direction southwest of Dover Strait (Fig. 12). This may be attributed to contaminated inputs but also to an increased adsorption of metal on SPM due to an increase of the organic fraction. In fact, zinc is known to be readily adsorbed on dead organic matter (Martin and Knauer, 1973). In the Celtic Sea, the high observed concentrations could be explained by reference to the essential role of zinc as a micronutrient for phytoplankton that constitutes the bulk of suspended matter in this area (*see* also the high Zn/Al

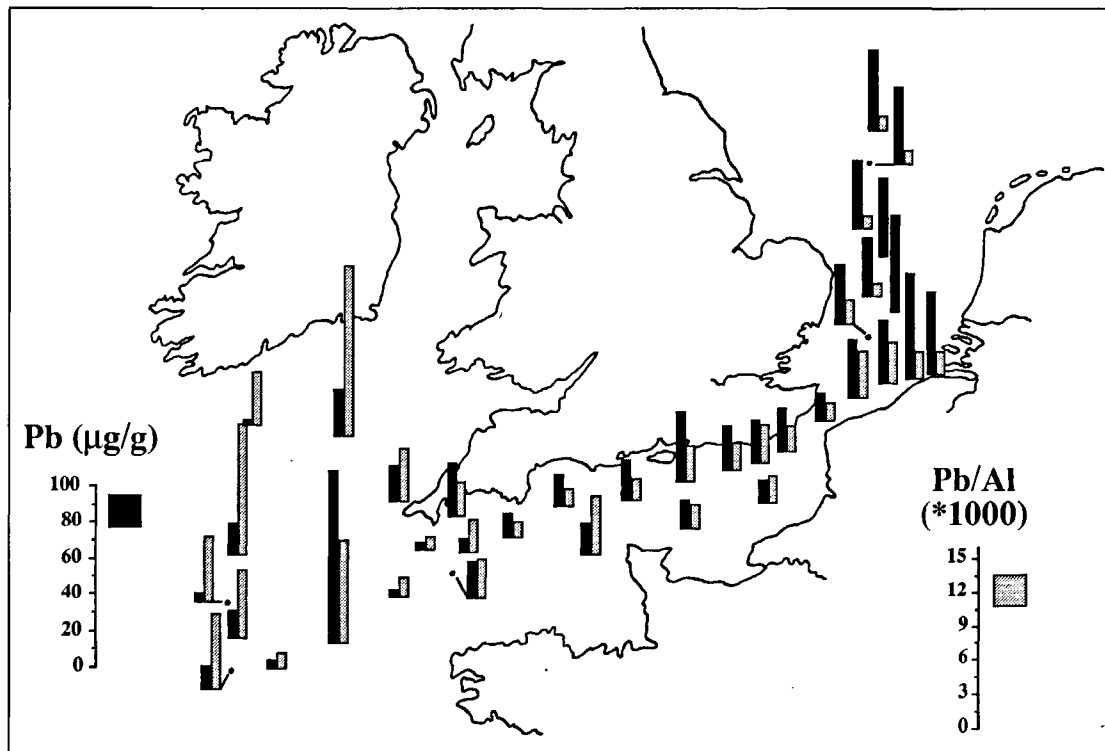


Figure 9

Pb: same as Fig. 6. Columns for Pb/Al ratios lower than 1×10^{-3} have not been drawn.

Pb : idem Fig. 6. Les barres des rapports Pb/Al inférieurs à 1.10^{-3} n'ont pas été représentées.

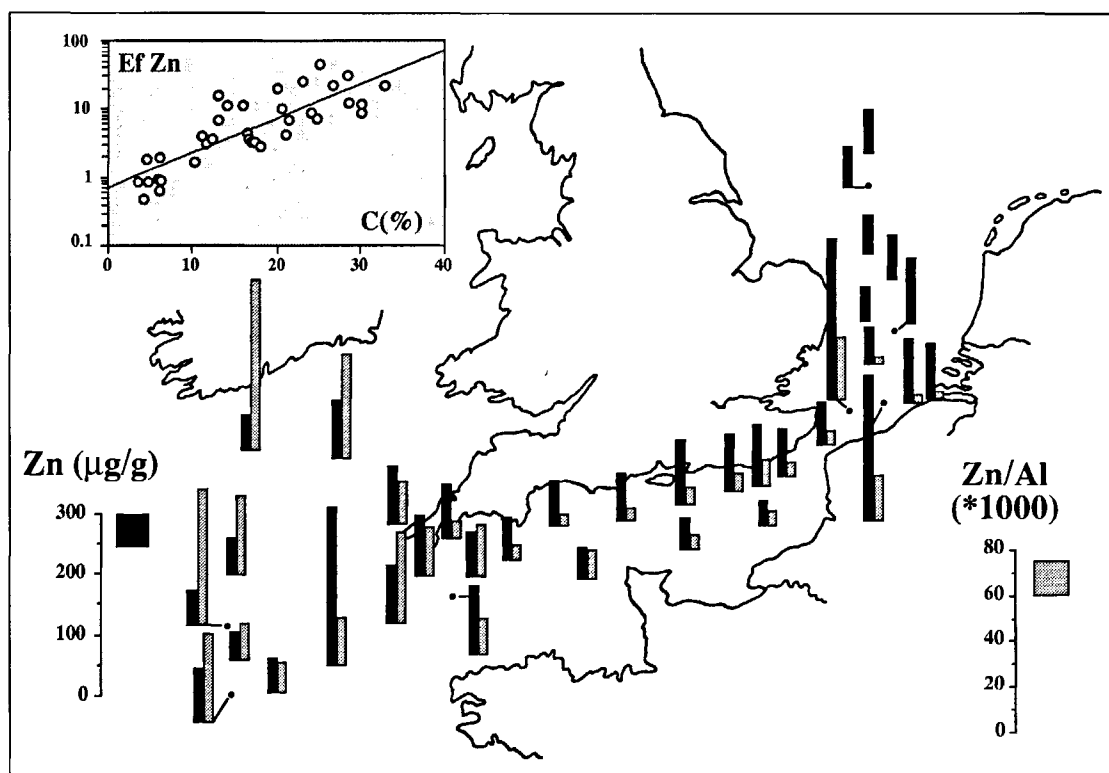


Figure 10

Zn: same as Fig. 6. Columns for Zn/Al ratios lower than 3×10^{-3} have not been drawn. Upper left corner: relationship between Zn enrichment factors (log scale) and C content in SPM.

Zn : idem Fig. 6. Les barres des rapports Zn/Al inférieurs à 3.10^{-3} n'ont pas été représentées. Coin supérieur gauche : relation entre les facteurs d'enrichissement en Zn (échelle log) et le contenu en C de la matière particulaire.

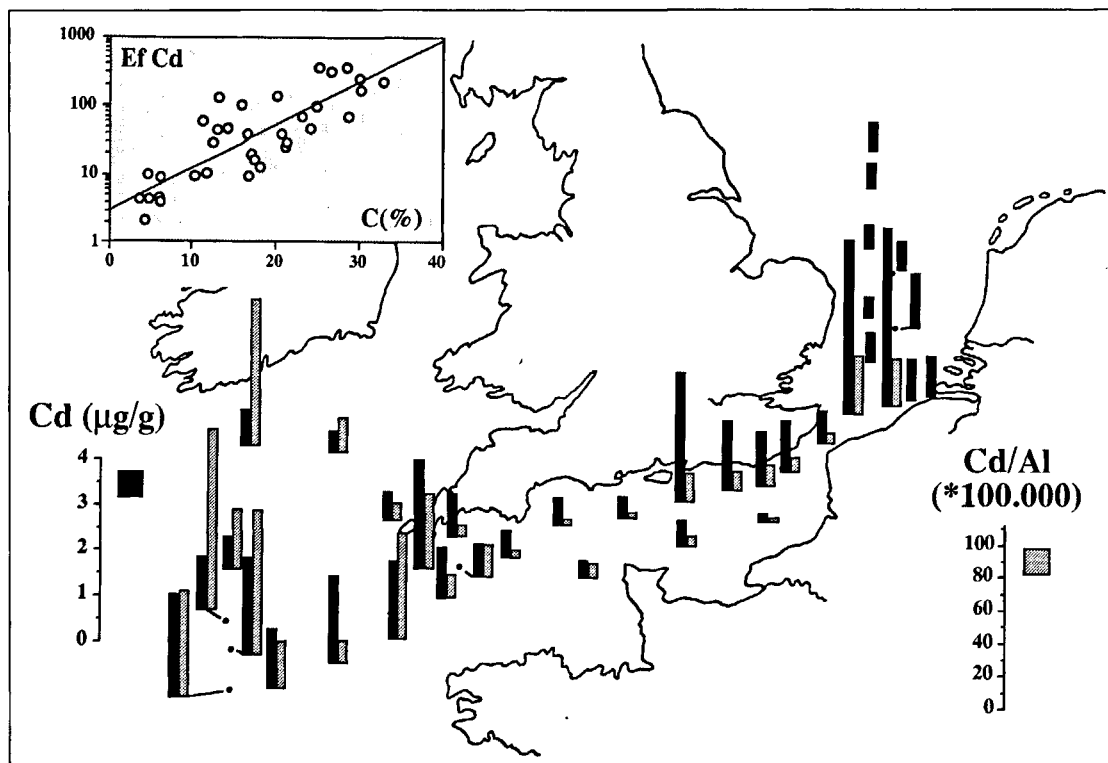


Figure 11

Cd: same as Fig. 6. Columns for Cd/Al ratios lower than 3×10^{-5} have not been drawn. Upper left corner: relationship between Cd enrichment factors (log scale) and C content in SPM.

Cd: idem Fig. 6. Les barres des rapports Cd/Al inférieurs à 3.10^{-5} n'ont pas été représentées. Coin supérieur gauche: relation entre les facteurs d'enrichissement en Cd (échelle log) et le contenu en C de la matière particulaire.

data). Binding of Zn on the organic fraction of SPM is moreover suggested when we consider the good correlation ($r^2=0.69$) between the Zn E_f factor and POC content (frame on Fig. 10).

Cadmium

Owing to its high toxicity, cadmium has been relatively well tracked in European coastal waters and several sets of data are available for either the dissolved phase (see *e.g.* Balls, 1985*b*; Duinker and Nolting, 1982; Kremling, 1983, 1985; Kremling and Pohl, 1989) or both the dissolved and particulate phases (separately or as a total). An overview of the latter data is presented in Table 3.

In the North Sea (Belgian coast excepted), we found Cd concentrations of about $0.4 \mu\text{g.g}^{-1}$ (about 3.5 ng.l^{-1}) in the SPM (Fig. 11, Tab. 2), in good agreement with the data of Fileman *et al.* (1991) but less than the data of Dehairs *et al.* (1985). Off the Belgian coast, values increase considerably, reaching up to $3.4 \mu\text{g.g}^{-1}$ near Zeebrugge; the maximum in terms of net amount is found at the Scheldt Mouth (about 67 ng.l^{-1}). This was also described by Baeyens *et al.* (1985, 1987) for the same area, and recent studies using biological indicators (Gobert *et al.*, 1992) strongly suggest that the Scheldt is an important source of Cd. At its riverine end member, concentrations can reach up to $20 \mu\text{g.g}^{-1}$ (Regnier and Wollast, 1993). These very high concentrations occasion less surprise when we consider that Bel-

gium is the third largest cadmium consumer in the world ($2700 \text{ tons.yr}^{-1}$) for her metallurgy.

In the Channel, Cd concentrations range from 0.4 to $2.9 \mu\text{g.g}^{-1}$ in front of the English coasts, with a maximum value off the Isle of Wight that corresponds to the highly industrialized basin round Southampton. The middle of the Channel seems to be less polluted, with values equal or less to $0.5 \mu\text{g.g}^{-1}$. The anthropogenic origin of cadmium in both the Channel and the Southern Bight is clearly demonstrated when looking to its E_f factors, the values of which are the highest of all the analyzed metals (Fig. 12).

Concentrations observed in the Celtic Sea are very similar to those of the western Channel although no direct pollution effect could be evoked. It must however be pointed out that Cd concentrations in SPM are high compared to Cd amounts (0.2 to 1.6 ng.l^{-1}), and thus could reflect a biological uptake by phytoplankton. This element is very soluble, rapidly recycled (Collier and Edmond, 1983), and has a nutrient-like behaviour in open oceanic waters and a unique behaviour with regard to its particulate concentrations (Sherrell and Boyle, 1992). As in the case of zinc, a good correlation ($r^2=0.70$) is observed when plotting Cd E_f factors against SPM carbon contents (frame on Fig. 11), suggesting adsorption by the organic fraction of suspended matter.

Relationships with physico-chemical parameters

In general, no correlation could be found between the distribution of any trace metal and temperature, salinity or

Table 2

Metal concentration in the particulate solid phase (mg or $\mu\text{g}\cdot\text{g}^{-1}$), particulate metal concentrations in sea water (μg or $\text{ng}\cdot\text{l}^{-1}$), and normalized ratios with respect to Al.

Concentrations en métaux dans la phase solide particulaire (mg ou $\mu\text{g}\cdot\text{g}^{-1}$), concentrations en métaux particulaires dans l'eau (μg ou $\text{ng}\cdot\text{l}^{-1}$), et rapports normalisés à l'aluminium.

Station	Al		Cd			Cr			Cu			Pb			Ti			Zn		
	mg/g	$\mu\text{g/l}$	$\mu\text{g/g}$	ng/l	Cd/Al*E3	$\mu\text{g/g}$	ng/l	Cr/Al*E3	$\mu\text{g/g}$	ng/l	Cu/Al*E3	$\mu\text{g/g}$	ng/l	Pb/Al*E3	$\mu\text{g/g}$	ng/l	Ti/Al*E3	$\mu\text{g/g}$	ng/l	Zn/Al*E3
1	30.7	226.2	0.4	3.2	1.4	48	355	1.6	83	611	2.7	41	299	1.3	1253	9225	41	53	394	1.7
2	32.1	363.4	0.4	4.0	1.1	44	497	1.4	76	860	2.4	39	443	1.2	1048	11854	33	51	579	1.6
3	31.9	268.9	0.4	3.1	1.1	46	384	1.4	46	388	1.4	35	292	1.1	1084	9126	34	49	416	1.5
4	65.8	653.8	0.4	4.3	0.7	54	539	0.8	58	577	0.9	40	393	0.6	939	9329	14	56	560	0.9
5	26.6	220.4	0.3	2.6	1.2	35	285	1.3	44	366	1.7	30	246	1.1	476	3940	18	43	358	1.6
6	69.9	319.6	0.8	3.8	1.2	82	374	1.2	199	909	2.8	49	225	0.7	637	2910	9	83	380	1.2
7	14.8	74.8	0.4	2.2	2.9	37	187	2.5	80	404	5.4	31	155	2.1	625	3163	42	46	235	3.1
8	20.9	2295.0	0.6	66.5	2.9	47	5178	2.3	61	6672	2.9	42	4658	2.0	900	98973	43	70	7750	3.4
9	22.8	2259.6	0.6	61.2	2.7	52	5110	2.3	23	2270	1.0	54	5328	2.4	965	95555	42	82	8103	3.6
10	11.2	45.9	3.3	13.5	29.5	31	128	2.8	25	101	2.2	40	163	3.6	366	1501	33	226	927	20.2
11	9.4	18.5	3.4	6.7	36.1	26	51	2.8	31	61	3.3	38	76	4.1	518	1019	55	263	517	27.9
12	10.6	20.4	0.6	1.2	5.6	15	28	1.4	22	42	2.0	17	33	1.6	410	787	39	64	123	6.0
13	13.2	36.6	1.1	3.1	8.4	25	68	1.9	53	147	4.0	31	86	2.3	550	1529	42	86	239	6.5
14	8.6	22.3	1.1	2.9	12.8	17	44	2.0	54	141	6.3	29	75	3.4	427	1110	50	105	272	12.2
15	3.7	13.9	0.1	0.4	2.7	14	52	3.7	10	38	2.7	9	34	2.4	171	648	47	24	92	6.6
16	12.5	14.6	1.4	1.6	11.2	20	23	1.6	51	60	4.1	30	35	2.4	482	564	39	100	116	8.0
17	16.6	22.3	2.9	3.9	17.4	29	39	1.7	41	55	2.5	53	70	3.2	907	1215	55	122	163	7.3
18	8.4	7.0	0.5	0.4	6.0	24	20	2.9	23	19	2.7	19	16	2.2	454	381	54	52	43	6.2
19	13.0	21.0	0.4	0.6	3.1	24	39	1.8	24	39	1.9	25	41	1.9	697	1129	54	76	122	5.8
20	2.4	4.6	0.2	0.4	8.5	17	32	7.1	14	27	6.0	12	24	5.2	73	142	31	30	58	12.8
21	13.5	21.3	0.5	0.8	3.7	22	34	1.6	14	22	1.0	20	31	1.5	478	755	35	71	112	5.2
22	10.8	21.7	0.5	1.0	4.6	17	34	1.6	27	55	2.5	15	30	1.4	363	730	34	65	130	6.0
23	2.0	2.7	0.4	0.5	19.7	18	24	9.0	19	25	9.5	6	8	2.9	80	105	39	45	59	22.4
24	9.7	15.7	0.7	1.1	7.2	66	107	6.8	32	51	3.3	30	48	3.0	344	557	36	76	122	7.8
25	5.1	8.6	0.7	1.2	13.8	21	36	4.2	23	40	4.6	18	30	3.5	214	364	42	81	138	15.9
26	3.0	5.4	1.4	2.5	46.1	56	99	18.4	22	38	7.1	3	6	1.1	81	143	27	64	114	21.2
27	1.4	2.7	0.9	1.8	65.2	32	62	22.9	12	24	8.8	3	5	1.8	73	142	53	56	109	40.4
28	9.7	10.3	1.3	1.4	13.4	69	73	7.1	97	102	10.0	88	93	9.1	452	480	47	198	210	20.5
29	1.8	2.5	0.5	0.7	27.9	11	15	5.9	6	8	3.2	3	3	1.4	33	46	18	24	33	13.4
30	1.0	1.8	0.9	1.6	88.2	19	33	18.7	19	34	19.0	7	11	6.5	47	82	46	39	68	38.2
31	2.2	2.5	1.5	1.6	64.7	28	31	12.4	24	27	10.9	14	15	6.1	18	20	8	35	39	15.7
32	0.4	0.2	0.4	0.2	111.1	25	13	69.2	50	26	137.8	2	1	5.8	18	10	50	22	11	59.7
33	1.3	0.8	0.5	0.3	35.8	265	156	197.4	31	19	23.4	16	9	11.6	34	20	26	46	27	34.4
34	0.4	0.3	0.4	0.3	90.9	26	17	59.5	31	20	70.7	2	1	4.8	19	12	43	33	21	75.7
35	1.0	1.0	0.2	0.2	20.8	59	60	61.3	27	27	27.8	15	15	15.1	40	41	42	45	45	46.4
36	3.7	4.6	0.4	0.5	10.9	49	62	13.4	27	34	7.3	17	22	4.6	178	224	48	69	87	18.9
crust*	69.3		0.2		28	71		1.0	32		0.46	16		0.23	3800		55	127		1.8
rivers*	94		1		1.1	100		1.1	100		1.1	100		1.1	5600		59	250		2.7

* Mean data from Martin & Meybeck, 1979.

nutrient (nitrates) concentrations for the whole domain. This is quite comprehensible given the complexity of water circulation in the area (especially in the Channel, Salomon and Breton, 1991), the number of local hydrological regimes and the importance of land inputs. Conservative behaviour could, however, be detected for some metals (Zn, Cu and Pb) in the Western Channel or in the Southern Bight, but we do not possess sufficient data to display this adequately. In the same way, the 'classical' relation between temperature and SPM $\delta^{13}\text{C}$ (Fontugne and Duplessy, 1981; Laane *et al.*, 1990) was not observed for similar reasons.

CONCLUSION

The distribution of organic carbon and nitrogen and of particulate trace metals in the Southern Bight of the North Sea, the English Channel and the Celtic Sea reflects well the origin of the SPM and permits distinction between the detrital fraction of continental origin and the biogenic material produced in the water column.

As may be expected, the relative importance of the biological fraction gradually increases from the North Sea towards north-eastern Biscay, as shown by POC, PON or

Table 3

Summary of previous trace metal determinations for the prospected area (only papers dealing with the particulate phase have been retained).
Aperçu des données antérieures de la littérature pour la zone étudiée (seuls les travaux traitant de la phase particulaire ont été retenus).

Authors	Sites	Phase	Al	Cd	Cu	Pb	Zn
Mart and Nürnberg, 1986	German Bight, NS	total		21-53 ng/l	104-536 ng/l	38-289 ng/l	
Balls, 1985a	Northern North sea	part.		1 ng/l	10 ng/l	1-6 ng/l	
Balls, 1985b	Eastern coast of UK	part.			10-50 $\mu\text{g}\cdot\text{g}$	0-75 $\mu\text{g/g}$	
Fileman <i>et al.</i> , 1991	Dogger Bank	part.	2.49 mg/g	0.38 $\mu\text{g/g}$	3.2 $\mu\text{g/g}$	2.1 $\mu\text{g/g}$	11.8 $\mu\text{g/g}$
Dehairs <i>et al.</i> , 1985	Central North Sea	part.	0.46 mg/g	2.0 $\mu\text{g/g}$	30 $\mu\text{g/g}$	36 $\mu\text{g/g}$	590 $\mu\text{g/g}$
	Southern Bight		12 mg/g	1.1 $\mu\text{g/g}$	18 $\mu\text{g/g}$	71 $\mu\text{g/g}$	305 $\mu\text{g/g}$
	Channel		7 mg/g	1.3 $\mu\text{g/g}$	23 $\mu\text{g/g}$	39 $\mu\text{g/g}$	433 $\mu\text{g/g}$
Duinker and Nolting, 1977	Southern Bight	part.	\approx 30 mg/g		25 $\mu\text{g/g}$		100 $\mu\text{g/g}$
Nolting, 1986	Southern Bight	part.		10 ng/l	365 ng/l		600 ng/l
Nolting and Eisma, 1988	Southern Bight	part.	\approx 30 mg/g	\leq 2 $\mu\text{g/g}$	\leq 100 $\mu\text{g/g}$	(< 300 $\mu\text{g/g}$)	(< 500 $\mu\text{g/g}$)
Baeyens <i>et al.</i> , 1985	Scheldt mouth	part.		110 ng/l	1100 ng/l	3500 ng/l	5100 ng/l
Regnier and Wollast, 1993	Scheldt mouth	part.	25-45 mg/g	\approx 1.5 $\mu\text{g/g}$	\approx 35 $\mu\text{g/g}$	\approx 70 $\mu\text{g/g}$	
Baeyens <i>et al.</i> , 1987	Belgian Coast	part.	4-20 mg/g	130 ng/l	2.6 $\mu\text{g/l}$	3.6 $\mu\text{g/l}$	9.3 $\mu\text{g/l}$
Danielsson <i>et al.</i> , 1985	Chanel + adjacent	total		12-25 ng/l	79-340 ng/l		125-660 ng/l

$\delta^{13}\text{C}$ distribution patterns. Concurrently, there is an opposite gradient in the importance of the lithogenic fraction from the Celtic Sea to the Southern Bight, as proven by Al, Ti or metal/Al ratio distributions.

Among the analyzed trace metals, differences in behaviour can be observed with respect to their distribution in suspended matter. Zinc and lead show almost similar concen-

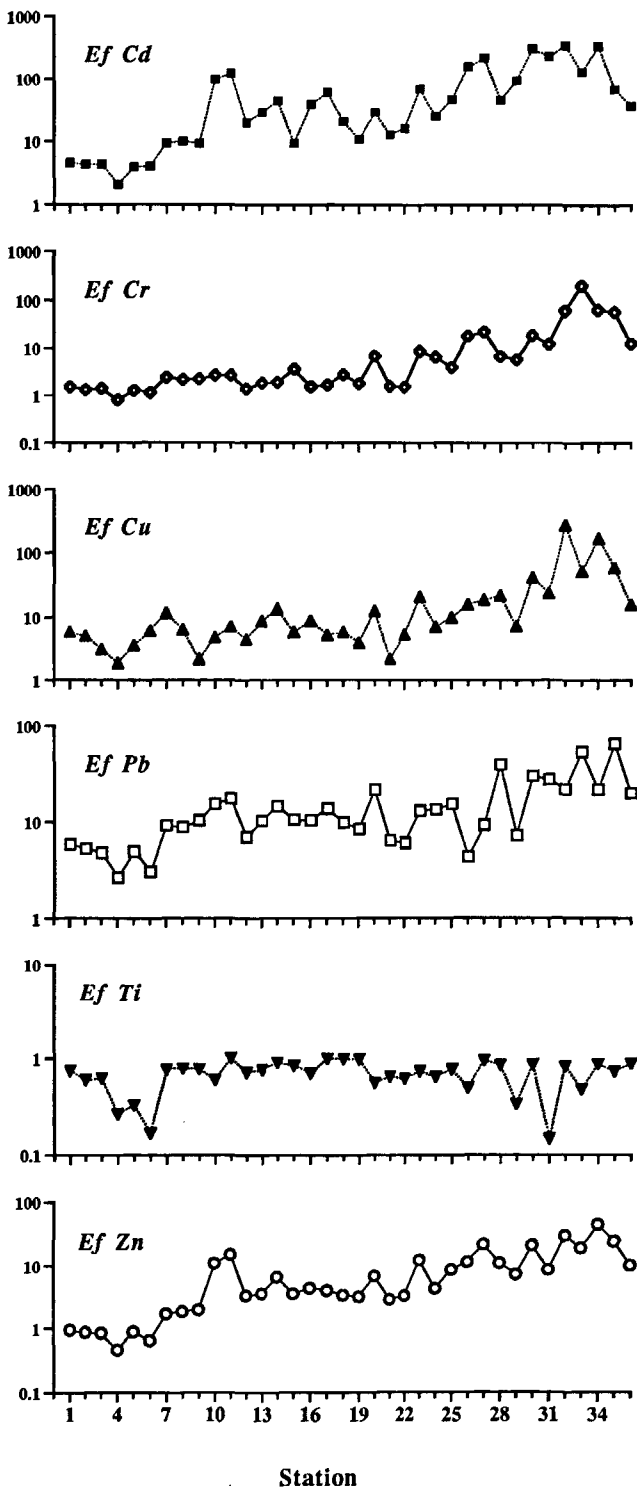


Figure 12

Distribution of metal enrichment factors (E_f - log scale) at the different sampling stations.

Distribution des facteurs d'enrichissement (E_f - échelle log) métallique aux différentes stations de prélèvement.

tration patterns (albeit with some local differences) and present maximum abundances in the vicinity of highly industrialized areas or near large estuaries: off Hampshire and Sussex (and to a minor extent off Cornwall) in the Channel, and in front of the Belgian and Dutch coasts in the North Sea. The respective actual inputs of the atmosphere and of rivers in the total amount of these metals in sea water is hardly computable from our data; nevertheless, Baeyens *et al.* (1985) have shown that, for *e.g.* the Belgian coast, they could be of the same order of magnitude.

The cadmium distribution pattern is quite different. Although high values are observed in polluted waters bordering on important human activity centres, other high concentrations in SPM are found far from direct anthropogenic influence, for example near the Little Sole Bank in the north of Biscay. These values, and the correspondingly high calculated enrichment factors, suggest a biological uptake of this metal in waters rich in organic SPM. Wollast and Loijens (1992), using radionuclides, have measured, for the same study area, high relative uptakes of trace metals by the particulate phase. Such a process might well be evoked to explain relatively high Cd (and Zn and Cr) amounts in SPM from oligotrophic waters and the relationships observed between the E_f factors of these metals and C contents of POM.

Copper distribution is more intricate as this metal is readily bound to organic matter, even of detrital origin. Its highest concentrations are thus observed in areas of riverine influence and in shallow waters where resuspension of benthic particles may affect the composition of surface layer SPM. But high Cu values are also noticed in phytoplankton-rich oceanic waters, suggesting that an active uptake by living matter occurs.

Finally, measurements of $^{13}\text{C}/^{12}\text{C}$ ratios in the SPM have shown that, although the precise source of some observed ^{13}C -enriched values is not elucidated, they could be used to trace land - or coast - originated as opposed to ocean-derived materials.

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